

Second Quarterly Report

on

STUDY OF USE OF AUXILIARY ELECTRODES IN SILVER CELLS

1 May, 1964 - 1 August 1964

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Advanced Technology Laboratories  
Schenectady, New York

for

Goddard Space Flight Center  
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## SUMMARY

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The primary objective of this program is to investigate the use of auxiliary electrodes in primary and secondary silver-zinc cells and to modify commercially available silver-zinc cells for testing by NASA-Goddard. Additional work areas include the continuation and the completion of testing of silver-cadmium cells with auxiliary electrodes remaining from Contract NAS 5-2817, and the investigation of electrochemical techniques for recombining hydrogen evolved from primary silver-zinc cells used in satellite power supply systems.

Project work for the quarter included testing of several types of auxiliary electrodes that do not contain platinum metal catalysts for oxygen recombination; testing of a non-magnetic auxiliary electrode containing platinum metal catalysts for hydrogen recombination; construction of a number of silver-cadmium cells with conventional auxiliary electrodes and placing six of the cells on continuous charge under voltage limiting conditions ( $1.52 \pm 0.01$  volts per cell); and designing a hydrogen combination cell for use in removing hydrogen from enclosed spaces.

The test results on the use of silver mesh and silver powder electrodes for oxygen recombination show that these electrodes are suitable for use in silver-zinc cells but at lower current densities than for the conventional auxiliary electrodes containing platinum metal catalysts. The more efficient platinum metal catalyst system cannot be used if the electrodes are coupled with the zinc electrode, as it promotes self-discharge of the zinc electrode.

The non-magnetic auxiliary electrode for hydrogen recombination is made using silver mesh and powder in place of nickel in the conventional electrode; platinum and palladium black are used as catalysts with a Teflon binder. Tests show that (after some initial problems on catalyst activity were solved) the electrode with silver substrate is suitable for use in cells for recombination of hydrogen.

The early behavior of the silver-cadmium cells on continuous overcharge shows a small initial rise in pressure which has been followed by a decrease in pressure. The voltages of the cells in the series pack of six cells have become equalized at the end of the second week of charging. This test is being continued. Additional modified silver-cadmium cells will be placed on cycling tests in the next quarter.

The design study of the hydrogen combination cell shows that cupric oxide is the optimum material to use in the cathode. A preliminary design shows that a hydrogen combination cell capable of removing hydrogen at the rate of 200 cc (STP) per hour for six months would weigh about 7.5 pounds.

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## 1.0 INTRODUCTION

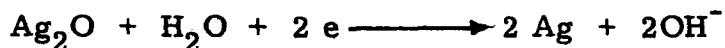
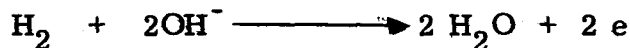
This report covers the work done during the second quarter of a twelve-month program to investigate the use of auxiliary electrodes in silver-zinc cells. Two additional work areas are the continuation and completion of cyclic tests of silver-cadmium cells with auxiliary electrodes from a previous contract (NAS 5-2817) and the investigation of the feasibility of recombining hydrogen evolved from a silver-zinc satellite power supply system by means of an electrochemical cell.

Of primary concern, in the application of auxiliary electrodes to silver-zinc cells, is poisoning the zinc electrode with platinum from the auxiliary electrode which catalyzes the self-discharge reaction of the zinc electrode:



It is believed that the danger of platinum migration to the zinc electrode is small since, (1) the binder of the electrode has been very effective in holding the catalyst in place and has shown no deterioration in electrodes used for 10-14 months; (2) the platinum is in a highly insoluble form and has shown no tendency to go into solution when the electrode is used at current densities below 50 ma/cm<sup>2</sup>; (3) the barriers used in silver cells for blocking silver migration are equally effective for platinum, since platinum compounds are more easily reduced or absorbed than silver.

Although the auxiliary electrode has been used primarily as an oxygen electrode in silver-cadmium applications, there is no basic reason for an auxiliary electrode being operated only as an oxygen electrode. It can also be operated as a hydrogen electrode. For use as a hydrogen electrode, the auxiliary electrode would be connected to the positive (silver oxide) electrode in use, the recombination reactions being:



With this type of auxiliary electrode operation, the cell should be designed to be negative plate limiting, so that hydrogen is preferentially evolved on charging. The use of a hydrogen recombination system is desirable for

silver-zinc cells, since there is an evolution of hydrogen during the cell stand and discharge that leads to pressure build-up in many applications.

The use of two auxiliary electrodes -- one for oxygen recombination which is attached to the negative electrode, and one for the recombination of hydrogen which is attached to the positive electrode -- is possible. The principal advantage of this dual system is that gassing of either hydrogen or oxygen would be taken care of. Also, the use of a platinum containing catalyst for the oxygen electrode is not needed thus removing the possibility of zinc electrode degradation by coupling through the external circuit. This non-platinum containing type of electrode was originally proposed for use in silver-cadmium cells, but was abandoned in favor of the currently used one which can recombine small amounts of hydrogen directly, since this property was useful and presented no problems in use in silver-cadmium cells.

Another potential problem area is the possible poisoning of the auxiliary electrodes by interactions with both silver and zincate ions present in the electrolyte phase of these cells. At present, there is no evidence that either will degrade the electrode for oxygen or hydrogen recombination. This aspect, however, is being investigated.

An outline of the program work content by tasks is given in Table I.

TABLE I  
Program Tasks

Task I - Silver-Cadmium Cells.

The 5.0 amp. hr. test cells from the previous contract (or new ones) with auxiliary electrodes will continue to be cycled at room temperature with periodic monitoring of cell capacity and continuous monitoring of cell pressure.

Task II - Silver-Zinc Cells.

Perform studies on the use of auxiliary electrodes for recombination of hydrogen and oxygen as a function of operating parameters to obtain design data to modify commercial silver-zinc cells of 3.0 amp. hr. capacity.

- A. Study the effect of auxiliary electrode materials on the self-discharge of the zinc electrode in both the electrically coupled and uncoupled condition.
- B. Study recombination of hydrogen during charge, stand, and discharge by an auxiliary electrode connected to the positive cell electrode.
- C. Study the recombination of oxygen during charge and stand on an auxiliary electrode when connected to the negative cell electrode.
- D. Study the effect of silver and zincate ions on the hydrogen and oxygen recombination by auxiliary electrodes.

Task III - Modification of Silver-Zinc Cells.

Incorporate auxiliary electrodes into fifty 3.0 amp. hr. commercially available silver-zinc cells.

Task IV - Hydrogen Recombination Cell.

Investigate the feasibility of electrochemical recombination of hydrogen evolved from silver-zinc satellite power supply systems. Cells employing AgO and CuO will be investigated initially.

## 2.0 WORK ACCOMPLISHED

The work during the second quarter was largely concerned with carrying out the initial parts of the work program established and started during the first quarter. This included the fabrication of test cells for obtaining design data for auxiliary electrodes to be used in modifying silver-zinc cells, and the fabrication of other test cells and equipment for carrying out the program. The accomplishments for the quarter are discussed by Tasks in the following sections.

### 2.1 Silver-Cadmium Cells - Task I

New test cells were constructed and put on test to obtain additional design and performance data. These cells are fabricated from Yardney YS-5 electrode packs consisting of four silver and five cadmium electrodes and the original separators. The auxiliary electrode was of the same material used previously, i. e. a nickel wire mesh coated with a thin layer of electrode catalyst containing platinum metals, plus a nickel powder electron collector and Teflon binder. The dimensions of the auxiliary electrode are the same as the dimensions of the YS-5 electrodes. The auxiliary electrode is placed against one of the two end cadmium electrodes with a Pellon 2505W Nylon separator between the two. The gas side of the auxiliary electrode is separated about 3/16 inch from the cell case by a piece of polyethylene grid (Vexar Plastic Netting, Vexar Division, E.I. du Pont de Nemours, Buffalo, N. Y., diamond pattern 4/4-30-90-PE-3). An additional 1/4 inch length of cell case has been provided to serve as electrolyte storage during cycling operation; wicks of Nylon separator were placed to extend from the bottom of original cell separators and the bottom of the reservoir. The test cells are potted in 1 inch of epoxy and are fitted with a pressure connection to either a pressure gauge or pressure transducer. A toggle valve is provided to permit connection of the gas system to external gas pumps or analysis equipment as desired.

The test cells were formed by completely filling the cell with 30% potassium hydroxide and allowing a 24 to 48 hour soak period to equilibrate the separators, then charging for 20 hours at 300 ma. constant current. The electrolyte level was then adjusted so that the bottom of the electrode pack was immersed in 1/8 inch of electrolyte. The cell was discharged at 2.5 amperes to a 1.0 volt cut off. The electrolyte level at the end of discharge was about 1/8 inch deep in the reservoir; this assures that the electrode pack separators are always wetted.

The first six cells made were cycled three times using the forming charge and discharge to determine capacity, charged fully and connected in series to form a 6-cell battery, and then placed on continuous overcharge at constant voltage of  $9.12 \pm 0.06$  volts or  $1.52 \pm 0.01$  volts per cell. The voltage across the battery alone is controlled; this arrangement allows the individual cell potentials to vary during overcharging. The purpose of this test is to determine the behavior of the cells on continuous overcharge such as would be experienced on satellites in a polar orbit. For the initial part of the experiment, the auxiliary electrodes are not connected with either electrode in the cell; this is to test the hypothesis that only a gas recombination catalyst is needed for cell operation under constant voltage charging to prevent excessive build up of gas pressure or loss of cell balance.

Table II shows the results of the capacity measurements for the cells; Table III shows the results for the first two weeks of the overcharging tests. The pressures and individual cell voltages are monitored daily; the charging current dropped to the nominal value of a few milliamperes at the end of this time. The voltage of the auxiliary electrode to cadmium is also monitored daily; the sign and the magnitude of the potential indicates whether an excess of hydrogen or oxygen is present. As of August 1, only oxygen was indicated in the test cells.

TABLE II

CAPACITY\* TESTS OF SILVER-CADMIUM CELLS

Cycle	C E L L					
	061501	061502	061503	061504	061505	061506
1	3.125	5.000	4.375	---	4.060	3.750
2	4.400	5.625	5.150	4.690	4.060	3.590
3	4.525	6.025	5.310	4.375	2.920	3.440

\* 300 ma charge for 20 hours, discharge at 2.5 amperes to 1.0 volt cut off.

TABLE III

CONTINUOUS CHARGE(1) CELL DATA

Day	C E L L						
	061501	061502	061503	061504	061505	061506	
P R E S S U R E (2)							
7/20	30 in.	30 in.	25 in.	18 in.	4 psi	30 in.	
7/21	30 in.	30 in.	15 in.	5 in.	10 psi	23 in.	
7/22	25 in.	28 in.	5 psi	5 in.	20 psi	20 in.	
7/23	5 in.	26 in.	12 psi	5 in.	23 psi	15 in.	
7/24	3 psi	25 in.	9 psi	5 in.	23 psi	12 in.	
7/27	8 psi	18 in.	6 psi	1 psi	17 psi	7 in.	
7/28	9 psi	12 in.	8 psi	2 psi	15 psi	5 in.	
7/29	11 psi	3 in.	5 psi	0 psi	14 psi	5 in.	
7/30	12 psi	2 psi	4 psi	2 psi	14 psi	4 in.	
7/31	13 psi	3 psi	2 psi	1 psi	12 psi	0 in.	
V O L T A G E S (3)						Charge (4)	
7/20	1.48	1.50	1.50	1.51	1.72	1.50	60
7/21	1.51	1.53	1.54	1.51	1.60	1.49	30
7/22	1.54	1.52	1.56	1.50	1.58	1.48	16
7/23	1.56	1.52	1.56	1.50	1.56	1.48	6
7/24	1.56	1.52	1.56	1.53	1.56	1.48	4
7/27	1.54	1.54	1.54	1.54	1.55	1.49	3
7/28	1.54	1.53	1.54	1.53	1.54	1.48	3
7/29	1.53	1.53	1.54	1.53	1.54	1.51	3
7/30	1.53	1.53	1.53	1.53	1.54	1.53	3
7/31	1.54	1.53	1.54	1.53	1.53	1.54	3

- (1) Constant voltage,  $9.12 \pm 0.06$  volts on battery ( $1.52 \pm 0.01$  volt/cell avg). Started 8:00 a.m. 7/20/64, readings taken at 4:00 p.m. each day.
- (2) Pressure in inches of vacuum or guage PSI.
- (3) Volts/cell using 1000 ohms/volt meter.
- (4) Charge current, milliamperes.

Additional test cells have been prepared for use in cycling tests. These tests are scheduled to start in the next quarter. The continuous charging tests will be interrupted in December to allow checking of the capacity of the test cells, and determination of cell changes if any.

## 2.2 Silver-Zinc Cells

This task is concerned with obtaining design data on the suitability of various auxiliary electrode compositions for hydrogen and oxygen recombination. Factors which will be evaluated are: the effect of auxiliary electrode materials on self-discharge of zinc electrode, rates of recombination of hydrogen and oxygen at various levels of gas pressure, and the effects of silver and zinc ions on the rate of recombination.

### 2.2.1 Self-discharge of Zinc Electrode

The composition of the conventional auxiliary electrodes for oxygen recombination was found to be unsatisfactory for this function in silver-zinc cells. The platinum contained in these electrodes promotes the rapid discharge of the zinc electrode when electrically connected through a low resistance load. In one test a zinc electrode from a 3.0 amp-hour Yardney silver-zinc cell (Model PM-3) was completely discharged in approximately 8 hours when connected to an auxiliary electrode through a one ohm load. The dimensions of the auxiliary electrode were the same as the dimensions of the electrodes in the PM-3 cell pack.

Auxiliary electrodes using platinum catalysts as for the conventional electrode but with different electron carriers and overall construction were found, as expected, to discharge zinc electrodes rapidly when connected to the zinc electrode. Connection of the conventional and special auxiliary electrodes containing platinum catalysts to the silver electrode does not induce evolution of oxygen from the silver electrode or hydrogen from the zinc electrode in the same cell.

Auxiliary electrodes using non-platinum metal oxygen electrode catalysts are being prepared for testing. These catalysts are not expected to promote hydrogen evolution from the zinc electrode as they are inert with respect to hydrogen catalysis. These catalysts are mixed oxides of the spinel type, the most effective of which is cobalt aluminate suspended in a silver powder matrix. Tests on these electrodes will be made in the next quarter.

### 2.2.2 Hydrogen Recombination Studies

These studies are being made with test cells composed of an auxiliary electrode and either a zinc or a cadmium electrode. During overcharging, the zinc or cadmium electrode evolves hydrogen which is reacted at the auxiliary electrode, in effect setting up the hydrogen cycle for cell overcharge. It has been found useless to use catalysts that do not use platinum metals for hydrogen recombination in cells, since the non-platinum catalysts such as Raney nickel are rapidly destroyed by oxygen, and thus cannot be subjected to oxygen during their life. This oxygen attack precludes their use in cells that may at times have oxygen evolved from the electrodes.

Conventional auxiliary electrodes employ a nickel mesh, a nickel powder electron collector mixed with platinum and palladium black powders as catalyst, and a Teflon binder. This structure is magnetic. Since there is considerable interest in a non-magnetic structure, we are exploring the use of silver mesh and silver flake powder in place of the magnetic nickel in hydrogen recombination electrodes. The pasting behavior of the non-magnetic material is poorer than for the nickel substrate, and the initial batches of electrodes have been inferior in behavior to the conventional electrodes. However, with experience and added trials, silver substrate electrodes have been prepared that compare favorably with the conventional electrode.

In the test, electrodes of the same cross section as the electrodes in Yardney 3 ampere hour silver zinc cells were used. The electrodes were assembled in the cells with nylon separators, electrolyte added and the cells charged to 50 milliamperes at charge up the negative electrode completely. Gas space behind the auxiliary electrode was free of electrolyte and ample gas passage between the working electrode and the auxiliary electrode was provided. The cells were provided with pressure connectors for monitoring pressure with a pressure transducer and taking gas samples. Initially, four each of cadmium and zinc cells with silver substrate auxiliary electrodes were made. These cells were purged after charging by evacuation and filling with hydrogen; then the cells were adjusted to various initial pressures of 700, 100 and 10 and zero millimeters of hydrogen absolute and sealed. The voltages of the electrodes, auxiliary to reference, was in the vicinity of 0.3 to 0.4 of a volt at this stage. The cells were then subjected to charging at 12.5 milliamperes and the pressure and auxiliary to reference voltage monitored. The cells showed negligible pressure rise or change in voltage at this charging rate over 48 to 72 hours of continuous charging. The charging rate was then increased to 25 milliamperes and the cells with 700 and 100 millimeter initial pressure of the cadmium series showed pressure rise with the auxiliary electrode, reference to voltage rising to over 1.5 volts. Gas analysis showed the presence

of oxygen in substantial amounts indicating that the platinum catalyst in the auxiliary electrode had failed. This indication was confirmed in later tests on these cells and electrodes. At 50 milliamperes charging rate, all the cells gave pressure rises and all of the auxiliary electrodes appeared to fail by oxidation. All the electrodes rose to about 1.5 volts with respect to the reference. An analysis of the gas in the cells shows substantial amounts of oxygen as well as hydrogen, indicating again the failure of the auxiliary electrode catalyst.

The initial cell tests were made using the early attempts to make a non-magnetic auxiliary electrode and were unsatisfactory. New tests using the improved auxiliary electrode in cadmium test cells have been made on two cells. The results show that operation at 50 milliamperes at 10 and 0 millimeters of hydrogen can be tolerated with the new electrodes without appreciable oxidation or other indication of failure of the auxiliary electrode. New test cells using auxiliary electrodes made of the conventional material as well as silver substrate will be made in the next quarter and tested. We feel that suitable non-magnetic auxiliary electrode material has been developed and this will be confirmed in the future tests.

### 2.2.3 Oxygen Recombination Studies

These studies are being made with test cells of similar construction to the hydrogen recombination cells except different auxiliary electrodes and working electrodes are used. The first cell tests were made using a nickel-hydroxide working electrode which was followed by several tests with silver electrodes. Electrode sizes and general construction followed that of the hydrogen recombination cell.

Nickel hydroxide test cells using a silver mesh auxiliary electrodes (Type Ag-079-2, Designers Metal Corporation) were made and tested. The cells were charged to complete the charge on the nickel hydroxide electrode, purged with oxygen and then sealed, one with 700 millimeters of oxygen, one with 100 millimeters of oxygen absolute. The cells were then charged at 12.5 milliamperes continuously for 48 to 72 hours. During the tests, the 100 millimeter initial pressure electrode showed some pressure rise during operation. At 25 milliamperes, the lower pressure cell definitely gassed and pressure rose to several pounds and increased continuously throughout the charging period. At 50 milliamperes, both cells gassed and pressure was increased.

The cell gases were analyzed and found to contain, as expected, considerable amounts of hydrogen as well as oxygen, indicating that the silver electrodes had evolved hydrogen at the higher charging rates in the absence of sufficient oxygen pressure. This behavior is expected at lower pressures of

oxygen since it is well known that the recombination rate of oxygen on silver is low. The evolution of hydrogen is confirmed by the auxiliary to reference electrode voltage measurements which show voltages above 1.85 volts when hydrogen is being evolved.

Test cells with silver powder auxiliary electrodes made by pasting silver powder (Handy & Harmon Silflake 130) with a Teflon binder, gave similar results to the silver mesh electrode except that, as expected, the carrying capacity of the electrode is considerably increased because of the extra surface area of silver exposed. With too high an auxiliary current, the electrodes gas hydrogen which is not recombined in the absence of a hydrogen recombination system. Test cells using silver powder auxiliary electrodes and silver working electrodes taken from the Yardney 3 ampere hour cells were tested and found to give reasonably good behavior. Cells containing 700 and 100 millimeters initial oxygen pressure showed no pressure rise during the operations up to 50 milliamperes although the cells with 10 and zero millimeters initial oxygen pressure showed more hydrogen evolution and pressure rises up to 15 to 20 lbs. to the square inch. At 50 milliamperes, pressure rose in the cells. The recombination rate of the silver powder electrodes is thus substantially lower than auxiliary electrodes using platinum catalysts. Work in the next quarter will be to test the test cells that were constructed but not tested by the end of the report period. These cells have auxiliary electrodes containing spinel catalysts in silver powder on silver mesh grids. In fuel cell tests, electrodes of this type gave much better behavior than silver mesh or silver powder alone as the electrode catalyst for oxygen.

#### 2.2.4 Silver and Zincate Ion Effects

The effect of these two ions, if any, on the recombination rates will be determined by employing auxiliary electrodes in complete cells. Test cells of this type will be constructed in the next quarter and put on test. This is felt to be a conclusive proof of operation of auxiliary electrodes in silver zinc cells and it is felt not necessary to run individual tests on the effects of these ions on the electrodes as originally planned.

#### 2.3 Hydrogen Combination Cell

The objective of this task is to assess the feasibility of electrochemically recombining the hydrogen evolved from a silver-zinc satellite primary power supply system. The nominal recombination capacity is to be 200 cc. of  $H_2$  per hour.

This function is presently performed by adsorption of the hydrogen on palladium. A primary goal is to reduce the weight of the system. The adsorption capacity of palladium at ambient temperature and one atmosphere partial pressure of hydrogen is approximately 177g Pd/g  $H_2$ .

Copper (II) oxide appears to be an attractive cathode material from the standpoint of electrochemical reactivity and mass equivalent weight. The equivalent weight for copper oxide is 40 g/g hydrogen.

Test cells using commercially available copper oxide electrodes (McGraw Edison Alkaline Battery Division) and a conventional auxiliary electrode as hydrogen electrode will be made and tested over a range of temperatures and current densities. An initial calculation of the cell has been made that indicates that a cell weighing about 7.5 pounds would be able to recombine 200 ml hydrogen per hour over a period of six months.

### 3.0 PROGRAM FOR NEXT QUARTER

Testing of the silver-cadmium cells on continuous charge will be continued; and cycling tests simulating a 90 minute orbit will be started on an additional set of cells.

Work on the use of the spinel catalyst for auxiliary electrodes to recombine oxygen will be carried out, and additional tests made on oxygen recombination as needed to evaluate electrode material.

Work on the non-magnetic and conventional auxiliary electrodes with platinum metal catalysts for hydrogen recombination will be carried out, and additional tests made on hydrogen recombination.

Construction of several hydrogen combination cells using copper oxide cathodes and hydrogen anodes will be carried out, and tests of the cells at various gas pressures made.

Test cells with silver, zinc, and auxiliary electrodes will be constructed and tests started if time allows.